



# A modified silicic acid (Si) and sulphuric acid (S)–ZrP/PTFE/glycerol composite membrane for high temperature direct hydrocarbon fuel cells

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## HIGHLIGHTS

- We report increased conductivity with Si in zirconium phosphate membranes.
- We report decreased conductivity with S in zirconium phosphate membranes.
- Si modified ZrP–glycerol membranes are suitable porous catalyst layer supports.

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## ABSTRACT

Composite membranes composed of modified S or Si–zirconium phosphate (ZrP), porous polytetrafluoroethylene (PTFE) and, glycerol (GLY) were synthesized in this work. ZrP was precipitated via the in-situ reaction of zirconium oxychloride ( $\text{ZrOCl}_2$ ) with phosphoric acid ( $\text{H}_3\text{PO}_4$ ). Silicic acid and sulphuric acid were introduced as additives to phosphoric acid with variable Si/P or S/P mass ratios in the acid solution/suspension. The modified membranes were investigated as electrolytes for direct hydrocarbon fuel cells operating at temperatures  $\sim 200^\circ\text{C}$ . The present work shows that adding a small amount of silicic acid to phosphoric acid enhanced the proton conductivity, i.e. by having a Si/P mass ratio of (0.01) in the acid solution/suspension, the Si–ZrP/PTFE/GLY membrane conductivity was  $0.073\text{ S cm}^{-1}$ . This value approached the conductivity of Nafion ( $0.1\text{ S cm}^{-1}$ ). The results also showed that adding sulphuric acid to phosphoric acid led to a significant decrease in the membrane's proton conductivity. SEM analysis results showed a porous structure of the Si–ZrP modified membranes. This porous structure combined with the high proton conductivity reported, would make them good candidates for catalyst layer supports in fuel cell applications.

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## 1. Introduction

Proton exchange membrane fuel cells (PEMFC) currently operate at temperatures around  $80^\circ\text{C}$  with pressures between 1 and 3 bar [1]. PEMFC are attractive for their several advantages including the high power density, and all solid construction. By far, the conventional perfluorosulfonic acid (PFSA) membrane (Nafion) is the most commonly used membrane in PEMFC.

The incentives for high temperature operation ( $T > 110^\circ\text{C}$ ) in PEMFC are, 1) increasing the reaction kinetics, 2) reduction and/or

the elimination of the liquid water accumulation inside the fuel cell, mainly at the cathode, and 3) heat generation at greater temperatures. The reduction of the liquid phase will diminish the diffusion resistance, thus, more molecules will have easier access to the reaction sites [2]. Elimination of water will diminish corrosion.

The proton conductivity of Nafion and similar PFSA membranes is known to be strongly dependent on the water content needed to solvate the proton of the sulfonic acid groups. Although increasing the temperature is beneficial in the operation of PEMFC, the membrane material is still one of the main obstacles. Temperatures greater than  $80^\circ\text{C}$  cause the PFSA (Nafion) membranes to dehydrate, i.e. a dramatic decrease in proton conductivity [2]. Therefore, alternative materials have been explored to replace the existing PFSA membranes. These membrane materials are made of

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sulfonated aromatic compounds, solution casted polymer membranes, inorganic–organic composite membranes, or acid base polymer materials [3].

Various studies have investigated the synthesis of sulfonated aromatic compounds for fuel cell applications. Examples are the work of Chikashige et al. [4], in which sulfonated poly (arylene ether) ionomers were prepared and, the work of Kang et al. [5], in which polybenzimidazole compounds were prepared. Other studies explored the synthesis of solution-cast polymer membranes such as the work of Kim et al. [6]. Extensive efforts aimed at modifying the existing PFSA membranes based on the procedure of Grot [7], to enhance their water retention properties. Grot proposed the incorporation of inorganic fillers in membranes. The result is an inorganic–organic composite membrane. The preparation methods for such membranes are variable. They include the in situ precipitation of the inorganic material within the polymer matrix, and the introduction of the inorganic material into the polymer dispersion.

Nafion membranes have been modified by the incorporation of metal hydrogen phosphates, such as zirconium phosphate (ZrP), a solid proton conductor [8,9], by the incorporation of silica [10], an inorganic compound, and by the incorporation of metal oxides particles [11]. In particular, the incorporation of silica in Nafion has received a considerable attention in the literature due to the hygroscopic nature of silica compounds. Examples are the work of Pereira et al. [12], in which a Nafion/mesoporous silica membrane was prepared, and the work of Ke et al. [13], where nano-sized Nafion/SiO<sub>2</sub> was formed in-situ by the sol–gel process.

Zirconium phosphate Zr(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (ZrP) is one example of an inorganic material that has the attractive characteristics of: 1) possessing proton conductivity and, 2) a layered structure permitting the passage of guest molecules, 3) having weak acidic groups; thus, allowing the exchange of the protons in the POH group with other cations [14]. As a result, the admitted cations accommodated within the layers are expected to cause a change in the interlayer distance depending on the size of the guest molecule. Other examples of inorganic materials in composite membranes are ZrO<sub>2</sub> and TiO<sub>2</sub>. These oxides have attracted attention of scientists due to their water uptake properties.

This work describes an improvement over our previous synthesis of Nafion-free ZrP/PTFE/glycerol (GLY) composite membranes [15]. It is aimed at modifying the ZrP PTFE/GLY membranes using a second acid, either sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) or silicic acid (SiO<sub>2</sub>·H<sub>2</sub>O). The modified S and Si–ZrP/PTFE/glycerol composite membranes were investigated as potential electrolytes for high temperature PEMFC. To our knowledge, this type of composite membranes, with this combination of electrolyte materials, has not been reported in literature. Phosphoric acid solutions (H<sub>3</sub>PO<sub>4</sub>) containing small amounts of either sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) or silicic acid (SiO<sub>2</sub>·H<sub>2</sub>O, or H<sub>2</sub>O<sub>3</sub>Si) were used to react with zirconium oxychloride (ZrOCl<sub>2</sub>·8H<sub>2</sub>O) to form modified ZrP. By having solutions, in which the acids are mutually soluble, it was expected that a small proportion of the phosphorous (P) atoms in the resultant ZrP could be replaced by either sulphur (S) atoms or silicon (Si) atoms. Therefore, it is expected that the incorporation of Si would result in zirconium phosphate (Zr(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O) material, and a minor fraction of Zr(H<sub>2</sub>SiO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O, thus, increasing the OH groups in the ZrP lattice. The incorporation of S on the other hand is anticipated to decrease the number of OH groups in the ZrP lattice by yielding a minor fraction of material that has the formula Zr(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O. Since the Grotthus mechanism of proton conduction [16], is proton hopping between either water molecules or OH groups, the proton conductivity was expected to increase with increasing the OH groups in the composite membranes. In this work, the following investigations were performed on the

composite membranes: 1) changes in the ZrP morphology upon the introduction of Si and S and, 2) the evaluation of the modified composite membranes for proton conductivity.

## 2. Experimental

### 2.1. Synthesis of S–ZrP/PTFE/glycerol and Si–ZrP/PTFE/glycerol composite membranes

Unlaminated Sterlitech PTFE films (with a nominal thickness of 50 µm and a nominal pore size of 0.22 µm) were used as the porous starting material in this work. Zirconium oxychloride, ZrOCl<sub>2</sub>·8H<sub>2</sub>O (Sigma Aldrich) was reacted with 85% o-phosphoric acid (Fisher Scientific) to produce zirconium phosphate, Zr(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O, ZrP according to the chemical reaction described in Eq. (1) [17].



Ethanol (anhydrous ethyl alcohol from Commercial Alcohols Inc.), glycerol (certified ACS, assay 99.7% from Fisher Scientific) and iso-propanol (HPLC grade, assay 99.8% from EMD) were obtained to prepare the alcoholic suspension of ZrOCl<sub>2</sub>·8H<sub>2</sub>O. ZrOCl<sub>2</sub>·8H<sub>2</sub>O suspension was prepared using 50 mL of ethanol, 2 mL of water, 150 mL of isopropanol and a specific amount of glycerol (GLY). GLY was added in order to vary the GLY/ZrP mass ratio in the composite membrane. The alcoholic suspension was placed on a stirring hot plate and vigorously mixed using a magnetic stirrer.

The PTFE film was first weighed, then placed between Teflon™ hoops. The Teflon™ hoops were attached to a mixer shaft. The stirred alcoholic suspension was heated at 70 °C, and then introduced into the pores of the PTFE film as the hoops rotated. It was dripped onto the top side of the PTFE porous film so that it was well distributed. Dripping was periodically stopped to allow the evaporation of alcohol while the membrane continued to rotate. The dripping was started again once the rotating membrane appeared to be dry. This procedure was repeated until the total amount of alcoholic suspension of ZrOCl<sub>2</sub>·8H<sub>2</sub>O was consumed. The resulting membranes were then immersed in H<sub>3</sub>PO<sub>4</sub> for 72 h, allowing reaction in Eq. (1) to take place. In subsequent experiments, the zirconium phosphates (ZrP) material was modified by adding either sulphuric acid or silicic acid to phosphoric acid. For example, SiO<sub>2</sub>·H<sub>2</sub>O (–80 mesh powder, from Sigma Aldrich) was added to phosphoric acid with variable quantities to study the effect of various Si/P mass ratios. At some Si/P mass ratios, silicic acid was in solution. However, the solubility of silicic acid in phosphoric acid is limited. The maximum amount observed to dissolve was 0.1 g SiO<sub>2</sub>·H<sub>2</sub>O in 20 mL of 85% H<sub>3</sub>PO<sub>4</sub>. In some experiments, silicic acid was in solution, however, at higher Si/P ratios, when the solubility limit was exceeded, part of it was in solution while the other part appeared in suspension. Sulphuric acid (A.C.S reagent from Fisher Scientific) was also used to modify the membranes. Specified volumes of sulphuric acid were added to phosphoric acid in such a way to vary the S/P mass ratio in the acid solution. The membranes were then immersed in the acid solutions for 72 h and then, were gently rinsed with de-ionized water and isopropanol (ratio of 50:50 by volume) followed by drying in the oven for 24 h at 120 °C.

A high temperature processing test was performed at 200 °C for a sample of a Si–ZrP/PTFE/GLY membrane. The sample was first cut, weighed then put in a tube furnace under a combination of heat treatment and elevated water vapour pressure for 30 min. H<sub>2</sub>O and argon were injected at a H<sub>2</sub>O/Ar molar ratio of 6, and y<sub>H<sub>2</sub>O</sub> = 0.86 (wet test). This H<sub>2</sub>O/Ar molar ratio is identical to the H<sub>2</sub>O/C<sub>3</sub>H<sub>8</sub> ratio in the direct propane fuel cell reaction where H<sub>2</sub>O is a reactant. The processed membrane sample was then re-weighed and placed in

a sealed non-porous Teflon bag and sent for electrochemical impedance spectroscopy (EIS) analysis.

## 2.2. Characterization of the S–ZrP/PTFE/glycerol and Si–ZrP/PTFE/glycerol composite membranes

Proton conductivity measurements were performed using electrochemical impedance spectroscopy (EIS) by the four probe method. A Parstat, 2273 instrument and PowerSuite 2.58, 2003 electrochemical software were used. The measurement was done over a frequency range of 1–100 kHz. As explained in our earlier work [15], the value of the real electrolyte resistance,  $R$ , was obtained from the intersection of the line on the Nyquist plot with the  $x$ -axis. The membrane thickness,  $d$ , was measured and the cross sectional area of the sample,  $A$ , was calculated. The proton conductivity ( $\sigma$ ) was obtained from Eq. (2) [18]:

$$\sigma = d/(R \times A) \quad (2)$$

The surfaces of the composite membranes were examined by scanning electron microscopy (SEM). SEM was performed using a JEOL JSM-7500F Field Emission Scanning Microscope. Some composite membrane samples were freeze-fractured using liquid nitrogen prior to SEM analyses to examine their cross sections. Further analysis for the composite membranes was performed using Fourier transform infrared spectrometer, FT-IR analysis, using an FT-IR Nicole 6700 Spectrometer equipped with a ZnSe plate. The spectra for the samples were recorded in the range 3000–800  $\text{cm}^{-1}$  at room temperature. Samples of composite membranes were also analyzed by XRD (X-ray diffraction) using a Philips PW 3710 instrument equipped with Ni-filtered and Cu K[alpha] radiation ( $\lambda = 0.15418 \text{ nm}$ ) operating at 45 kV and 40 mA.

## 3. Experimental results

### 3.1. SEM observations and morphology studies of composite membranes

Fig. 1 shows SEM images for the unmodified ZrP/PTFE/GLY, and the Si or S modified composite membranes, and, compares them based on their top view. The composite membranes were all synthesized at a GLY/ZrP mass ratio of 0.4. The Si/P and the S/P mass ratios were 0.004 in the phosphoric acid–silicic acid (solution) for the modified membranes. SEM images show the ZrP material covering most of the pores of PTFE with some strands of the PTFE polymer still observable. SEM image (a) presents an unmodified ZrP/PTFE/GLY composite membrane, whereas images (b) and (c) of the same figure show a modified, Si–ZrP/PTFE/GLY and S–ZrP/PTFE/GLY composite membranes respectively. Careful examination of image (a) in Fig. 1 reveals the formation of nearly spherical ZrP particles, in the size range of 250–500 nm. Further examination of images (b) and (c) shows a visible change in the formed ZrP material's morphology. It is apparent that the addition of silicic acid into phosphoric acid caused a change in the produced ZrP particle size and shape. Plate-like ZrP particles of nearly 1  $\mu\text{m}$  in size were observed in image (b) for the Si-modified membranes. The particle size for the S-modified membranes also varied in the range of 1–5  $\mu\text{m}$  in some regions, as seen in image (c), with much less coverage observed than that appeared in images (a) and (b).

In general, the morphology of the Si-modified composite membranes changed from being nearly spherical in all regions, into an assortment of plate-like ZrP material of 1  $\mu\text{m}$  in size. The S-modification of ZrP also caused a change in morphology. This change in morphology was also accompanied by a change in proton

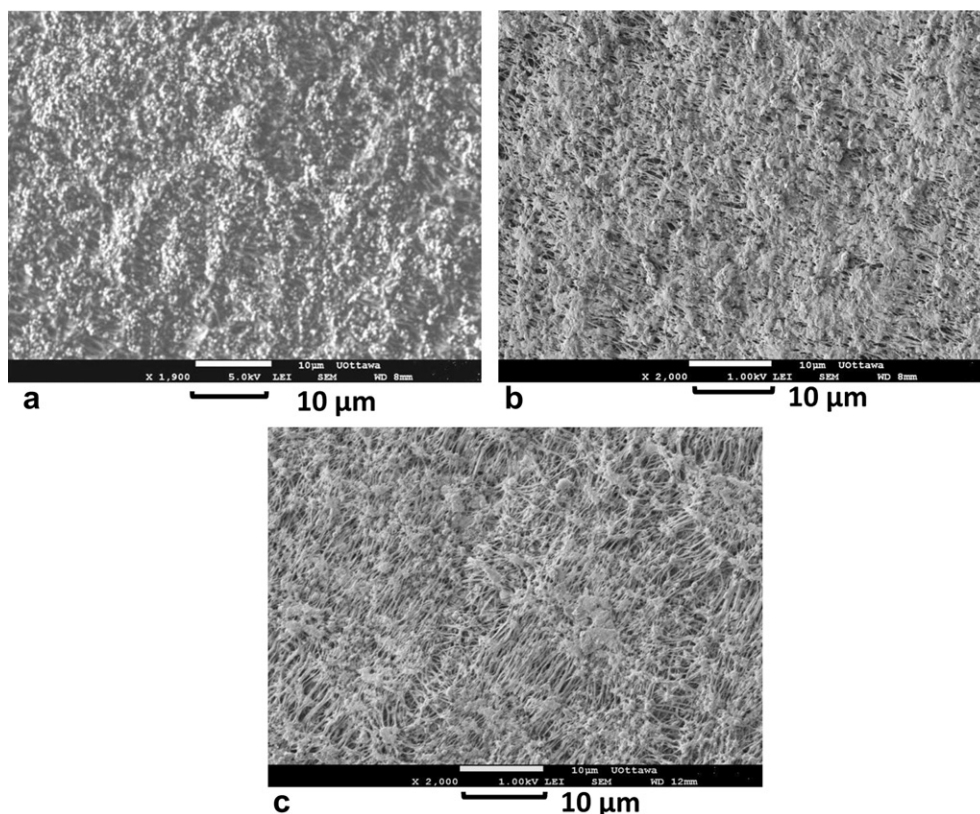


Fig. 1. SEM images for composite membranes, all at a GLY/ZrP mass ratio of 0.4. (a) An unmodified ZrP/PTFE/GLY membrane, (b) Si–ZrP/PTFE/GLY membrane with a Si/P mass ratio of 0.004 and (c) a S–ZrP/PTFE/GLY membrane at a S/P mass ratio of 0.004.

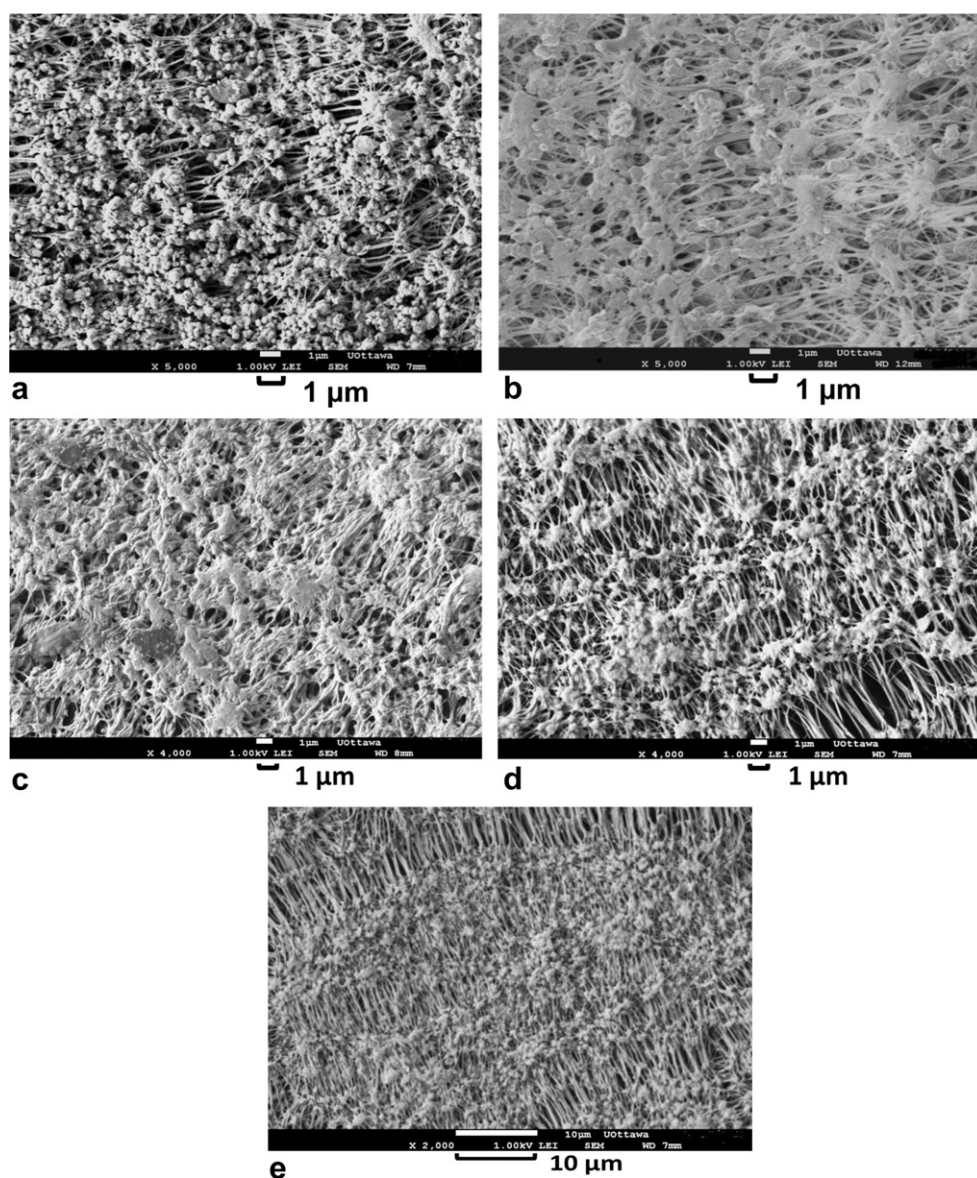


conductivity for both, the Si-modified ZrP/PTFE/GLY and the S-modified ZrP/PTFE/GLY membranes.

The effect of varying the Si/P mass ratios is shown in Fig. 2. All ZrP/PTFE/GLY composite membranes were prepared, at a GLY/ZrP mass ratio of 0.2. The Si/P mass ratios were varied from 0.0 to 0.02. SEM images in Fig. 2 show a top view for the composite membranes. Image (a) shows an unmodified ZrP/PTFE/GLY membrane (Si/P = 0.0). The ZrP particles appear to be nearly spherical in shape, in the size range of 300–600 nm. Image (b) shows a Si–ZrP/PTFE/GLY at a Si/P = 0.004 in the phosphoric acid–silicic acid (solution). At this Si/P ratio, all the silicic acid was soluble in phosphoric acid. It can be seen that the shape and size of the Si–ZrP material has changed from nearly spherical particles into a plate-like particles of a 1  $\mu$ m average size. Image (c) shows a Si–ZrP/PTFE/GLY membrane with a Si/P = 0.01 in the phosphoric acid–silicic acid suspension. At this Si/P ratio, some of the silicic acid was in solution, and some of it appeared in suspension. Additional changes in particles morphology were observed. Larger size ZrP material appeared,

having a flaky shape with an average size of 2  $\mu$ m. This noticeable change in size and morphology was accompanied by a change in the proton conductivity. Images (d) and (e) show a Si–ZrP/PTFE/GLY membrane with a Si/P = 0.02 in the phosphoric acid–silicic acid suspension. A plate like material continued to appear but it was evident that adding more silicic acid has resulted in much less coverage on top of the composite membrane. Further examination of image (d), shows strands of the polymer appeared to be entirely uncovered by the proton conducting material in some regions whereas the particles appear to agglomerate in other regions. It could be explained as a phase separation phenomenon as reported in literature for silica containing membranes. Lin et al. [19] reported phase separation in Nafion®/–SO<sub>3</sub>H functionalized mesoporous silica composite membranes. Changes in proton conductivities were also observed for these Si-modified composite membranes, as shall be discussed in Section 3.2.

Fig. 3 shows the SEM results for the Si–ZrP/PTFE/GLY membrane with a Si/P = 0.01, that had some silicic acid in suspension. Images (a)

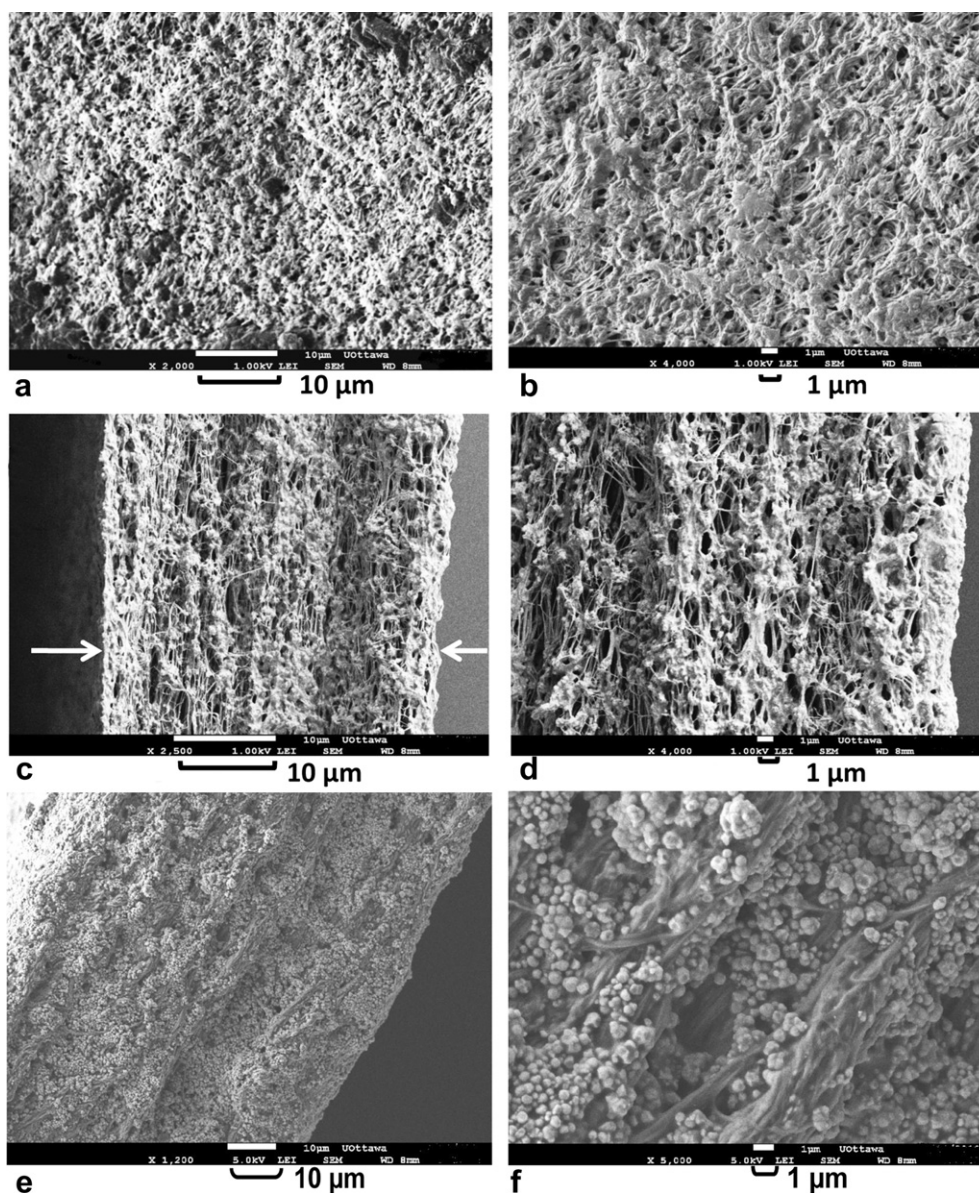


**Fig. 2.** SEM images for ZrP/PTFE/GLY composite membranes, all at a GLY/ZrP mass ratio of 0.2, variable Si/P mass ratios, (a) ZrP/PTFE/GLY membrane (Si/P = 0.0), (b) Si–ZrP/PTFE/GLY membrane Si/P = 0.004 (silicic acid is completely dissolved in phosphoric acid), (c) Si–ZrP/PTFE/GLY at Si/P = 0.01 some silicic acid is in suspension in phosphoric acid, (d) and (e) are for Si–ZrP/PTFE/GLY at a Si/P = 0.02, some silicic acid is in suspension in phosphoric acid.

and (b) show top view for the membrane at a different location than that appeared in Fig. 2(c). This figure confirms the changes in morphology and coverage observed in Fig. 2. Images (c) and (d) of Fig. 3 are a cross-sectional view of this composite membrane and they show the following: 1) the ZrP material appears to be suspended along the cross section of the highly porous support (PTFE), 2) the ZrP morphology appears to be different within the cross section (nearly spherical particles of  $\sim 300$  nm in diameter) compared to the (plate-like) particles observed on the top, and, 3) the intersections of the polymer strands appear to have been nucleation sites for the ZrP material with particles aggregation observed in some regions. A cross-sectional SEM view of the unmodified ZrP/PTFE/GLY composite membranes was shown in our previous work [15]. It is also shown in images (e) and (f) of Fig. 3. It appears to be quite different than the open structure shown in images (c) and (d). Instead, our previous work results showed a densely packed cross-sectional view with the spherical nano-scale ZrP material.

### 3.2. Proton conductivity of the Si–ZrP/PTFE/GLY and S–ZrP/PTFE/GLY composite membranes

The proton conductivities of the S and Si–ZrP/PTFE/GLY composite membranes were measured by EIS. The Nyquist plot obtained for the Si–ZrP/PTFE/GLY is shown in Fig. 4. In the same figure, the resistances of the Si–ZrP/PTFE/GLY (Si/P = 0.004) and the ZrP/PTFE/GLY composite membranes are compared. Both composite membranes were prepared having a GLY/ZrP mass ratio of 0.2. Both resistances obtained from the Nyquist plot, were used in Eq. (2) to calculate the proton conductivity. The results show that there is a decrease in the composite membrane resistance from  $0.41 \Omega$  to  $0.37 \Omega$  upon the addition of a small amount of silicic acid into phosphoric acid. The decrease in the composite membrane resistance led to an enhancement in proton conductivity. A conductivity of  $0.056 \text{ S cm}^{-1}$  value was obtained for the Si–ZrP/PTFE/GLY composite membrane, as opposed to a  $0.045 \text{ S cm}^{-1}$  for



**Fig. 3.** SEM images for a Si–ZrP/PTFE/GLY composite membrane, at a GLY/ZrP mass ratio of 0.2 and a Si/P mass ratio of 0.01 (some silicic acid is in suspension in the phosphoric acid). Images (a) and (b) are top view images. Images (c) and (d) are cross-sectional view images obtained by freeze-fracture. Edges of the membrane are indicated by the arrows in image (c). Images (e) and (f) are cross-sectional view images of the unmodified ZrP/PTFE/GLY composite membranes shown in our previous work [15].



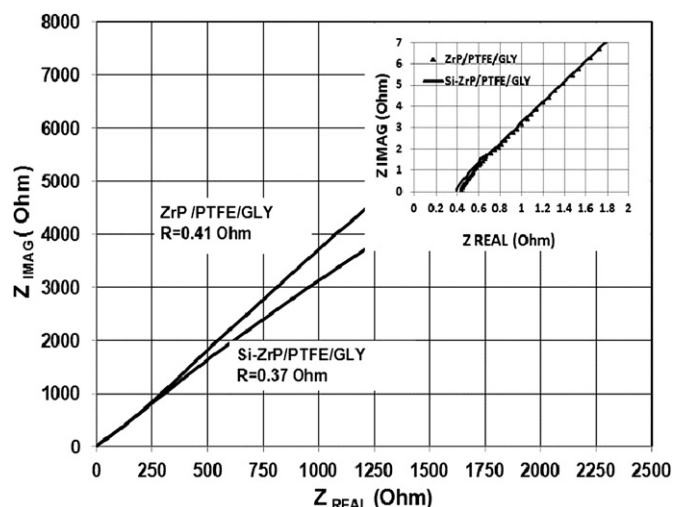


Fig. 4. Electrochemical impedance spectroscopy pattern for an unmodified ZrP/PTFE/GLY membrane and a Si-ZrP/PTFE/GLY composite membrane, both at a GLY/ZrP mass ratio of 0.2, and Si/P mass ratio of 0.004 in the phosphoric acid–silicic acid (solution).

the ZrP/PTFE/GLY membranes, i.e., an enhancement of 24% in proton conductivity.

The proton conductivity of the S-modified composite membrane (S-ZrP/PTFE/GLY) was also measured by EIS. The Nyquist plot in Fig. 5 compares the resistances of the ZrP/PTFE/GLY composite membrane and the S-ZrP/PTFE/GLY composite membrane. Both membranes were prepared at a GLY/ZrP mass ratio of 0.4, and the composite membrane modified with sulphuric acid ( $\text{H}_2\text{SO}_4$ ) had a S/P mass ratio of 0.004. It is evident that the addition of sulphuric acid caused an increase in the composite membrane resistance. The resistance increased from 1  $\Omega$  for the ZrP/PTFE/GLY membrane to 4.5  $\Omega$  for the S-ZrP/PTFE/GLY membrane. This increase in resistance resulted in a decrease in proton conductivity. The proton conductivity decreased from 0.02  $\text{S cm}^{-1}$  to 0.0044  $\text{S cm}^{-1}$  for the S-ZrP/PTFE/GLY membrane. The effect of sulphuric acid was further investigated at a S/P mass ratio of 0.54. The EIS measurements (not shown here) determined a resistance of 28  $\Omega$ , hence, a conductivity of  $6.49 \times 10^{-4} \text{ S cm}^{-1}$ , i.e. significant decrease in proton conductivity.

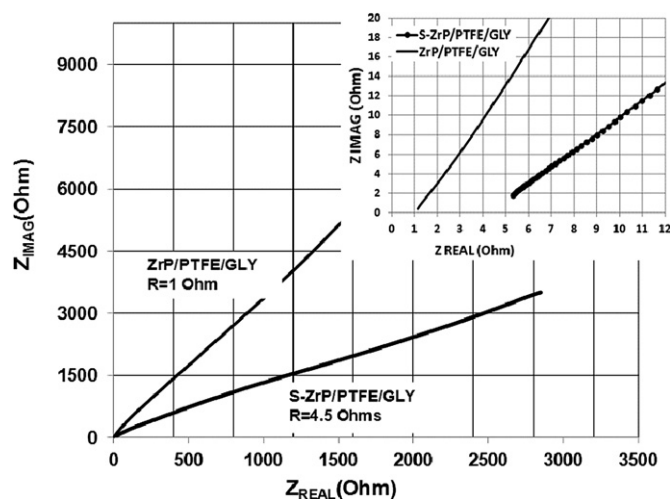


Fig. 5. Electrochemical impedance spectroscopy pattern for an unmodified ZrP/PTFE/GLY membrane and a S-ZrP/PTFE/GLY composite membrane, both at a GLY/ZrP mass ratio of 0.4, and S/P mass ratio of 0.004 in the phosphoric acid–silicic acid solution.

A comparison of the proton conductivity for the three types of the composite membranes is shown in Fig. 6. The GLY/ZrP mass ratio was 0.4 and the Si/P and, S/P mass ratios were 0.004, i.e. silicic acid was soluble at these conditions. The Si-ZrP/PTFE/GLY composite membrane showed the highest proton conductivity. The value of proton conductivity was improved from 0.02  $\text{S cm}^{-1}$  (for the ZrP/PTFE/GLY membranes, at GLY/ZrP = 0.4) to 0.027  $\text{S cm}^{-1}$  upon the modification with silicic acid. This increase in proton conductivity is anticipated to be due to the increase in the number of OH groups as previously discussed.

The effect of silicic acid addition at larger Si/P mass ratios was also investigated. As the Si/P ratio increased, the solubility limit of silicic acid in phosphoric acid was exceeded. At Si/P ratios larger than 0.004, a portion of silicic acid was soluble and some was still suspended in  $\text{H}_3\text{PO}_4$ . The results are shown in Figs. 7 and 8.

The new results for the Si-ZrP/PTFE/GLY composite membranes conductivity are shown in Fig. 7 as a function of the GLY/ZrP mass ratios. The new results are compared with results that were previously published for the unmodified membranes [15]. The maximum proton conductivity was reported at a GLY/ZrP mass ratio of 0.2 for both sets of composite membranes. It can be seen that there was a noticeable enhancement in proton conductivity upon the addition of silicic acid at all GLY/ZrP mass ratios. For example, the ZrP/PTFE/GLY composite membrane of 0.2 GLY/ZrP ratio, possessed a proton conductivity of 0.045  $\text{S cm}^{-1}$ , whereas the modified (Si-ZrP/PTFE/GLY) composite membrane (prepared at the same GLY/ZrP mass ratio 0.2) possessed a higher proton conductivity of 0.056  $\text{S cm}^{-1}$ .

A sample of the Si-ZrP/PTFE/GLY composite membrane (soluble silicic acid, Si/P = 0.004, and GLY/ZrP = 0.2, open triangle symbol) was processed at 200  $^{\circ}\text{C}$  and a  $\text{H}_2\text{O}/\text{Ar}$  molar ratio of 6, and  $y_{\text{H}_2\text{O}} = 0.86$  (a wet test = the inlet conditions of a direct hydrocarbon fuel cell). EIS analysis for this sample showed a slight decrease in proton conductivity, from 0.056  $\text{S cm}^{-1}$  to 0.046  $\text{S cm}^{-1}$  (shown as the solid triangle), i.e., a decrease in conductivity of only 24%. In comparison, the conductivity of Nafion 117 membranes at 120  $^{\circ}\text{C}$  and relative humidity (RH) of 95% is 0.013  $\text{S cm}^{-1}$  [20], and the conductivity of Nafion-silicate (NF-Si), and Nafion zirconium phosphates (NF-ZrP) at 130  $^{\circ}\text{C}$  and 28.8% RH is  $1.27 \times 10^{-3}$  and  $1.53 \times 10^{-3} \text{ S cm}^{-1}$  respectively [17]. After the 20% decrease in proton conductivity caused by the wet test, the proton conductivity for the Si-ZrP/PTFE/GLY composite membrane was still an order of magnitude larger than that of Nafion at comparable conditions.

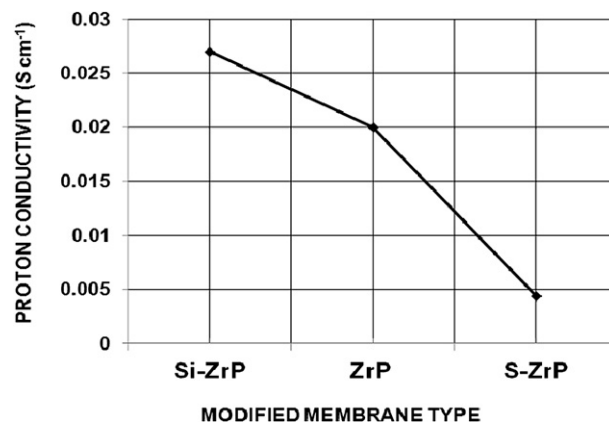


Fig. 6. Comparison between the three types of membranes, the ZrP/PTFE/GLY, the Si-ZrP/PTFE/GLY and the S-ZrP/PTFE/GLY in terms of proton conductivity. All were prepared at a GLY/ZrP mass ratio of 0.4 and Si/P, or S/P mass ratio of 0.004 in the acid solution.

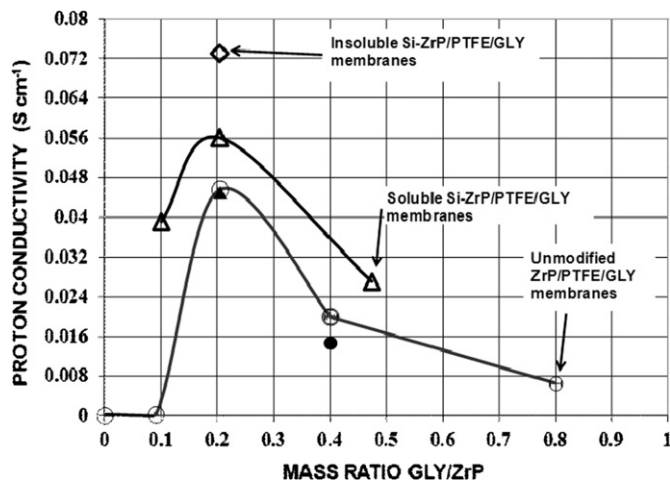


Fig. 7. Change of proton conductivity ( $\sigma$ )  $\text{S cm}^{-1}$  versus glycerol (GLY)/ZrP mass ratio. Open circles present the unmodified ZrP/PTFE/GLY composite membranes. Triangles: represent the Si-ZrP/PTFE/GLY composite membranes, Si/P mass ratio = 0.004 (silicic acid was completely soluble). Solid symbols represent the 200 °C wet test result of proton conductivity ( $\sigma$ )  $\text{S cm}^{-1}$ . Diamond symbol represents the Si-ZrP/PTFE/GLY composite membrane, Si/P mass ratio = 0.01 (some silicic acid was in the form of suspended particles).

The conductivities of the Si-ZrP/PTFE/GLY membranes were investigated as a function of their Si/P mass ratios. The results are shown in Fig. 8. The GLY/ZrP mass ratio was kept constant at 0.2, because the highest conductivity value obtained in Fig. 7 was obtained at this GLY/ZrP mass ratio. As the Si/P mass ratio increased, proton conductivity ( $\sigma$ ) also increased. As previously stated, up to a Si/P mass ratio of 0.004, silicic acid was still in solution. The maximum proton conductivity 0.073  $\text{S cm}^{-1}$  was obtained at a Si/P mass ratio of 0.01. When some of the silicic acid was present as insoluble particles, at Si/P mass ratios in the range of ( $0.004 < \text{Si/P} \leq 0.01$ ), additional proton hopping paths were provided by the surfaces of the hydrophilic  $\text{SiO}_2 \cdot \text{H}_2\text{O}$  suspended particles. At Si/P mass ratios larger than 0.01, the conductivity decreased reaching a value of 0.051  $\text{S cm}^{-1}$  at a Si/P mass ratio of 0.02. This decrease in conductivity can be explained by the morphology studies previously presented in Fig. 2(d) and (e) for this membrane. Upon the addition of more silicic acid (i.e. Si/P mass ratio = 0.02), poor coverage, more voids, and agglomeration of particles in some regions were obtained. Hence, it led to a decrease in proton conductivity.

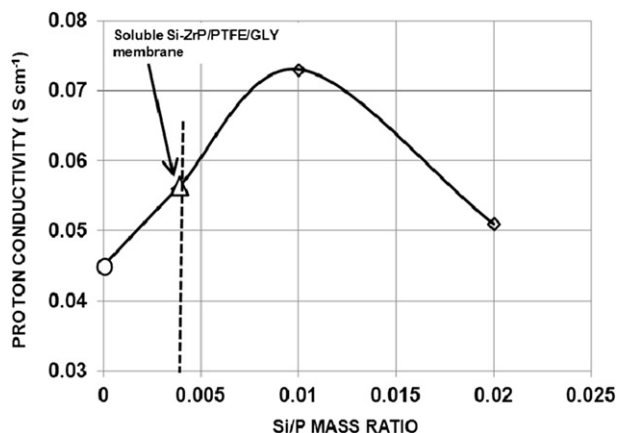


Fig. 8. Change of proton conductivity ( $\sigma$ ) with the Si/P mass ratio for the Si-ZrP/PTFE/GLY membrane at constant GLY/ZrP mass ratio of 0.2 (Si/P mass ratios larger than 0.004 contained insoluble portion of silicic acid in  $\text{H}_3\text{PO}_4$  as indicated by the dashed line.).

Table 1

Summary of conductivity results ( $\sigma$ ) in  $\text{S cm}^{-1}$  for the modified composite membranes.

Composite membrane type	$\sigma$ [ $\text{S cm}^{-1}$ ]	Mass ratio [GLY/ZrP]	Mass ratio [Si/P or S/P]
ZrP/PTFE/GLY	0.02	0.4	0
Si-ZrP/PTFE/GLY	0.027	0.4	0.004
S-ZrP/PTFE/GLY	0.0044	0.4	0.004
ZrP/PTFE/GLY	0.045	0.2	0
Si-ZrP/PTFE/GLY	0.056	0.2	0.4
Si-ZrP/PTFE/GLY	0.073	0.2	0.01
Si-ZrP/PTFE/GLY	0.051	0.2	0.02

The addition of silicic acid ( $\text{SiO}_2 \cdot \text{H}_2\text{O}$ ) to phosphoric acid, i.e. at Si/P mass ratios larger than 0.004, resulted in both soluble  $\text{SiO}_2 \cdot \text{H}_2\text{O}$  and suspended particles of  $\text{SiO}_2 \cdot \text{H}_2\text{O}$ . The presence of  $\text{SiO}_2 \cdot \text{H}_2\text{O}$  in solution improved water retention properties due to its hydrophilic nature. As previously discussed, by having  $\text{SiO}_2 \cdot \text{H}_2\text{O}$  in solution, some of the P atoms in ZrP might have been replaced by some of the Si atoms. Hence, increasing the number of OH groups, and, providing more paths for the protons to hop. Therefore, the proton conductivity increased. The further enhancement in proton conductivity upon the addition of  $\text{SiO}_2 \cdot \text{H}_2\text{O}$  in excess (of Si/P mass ratios = 0.01) might have been caused by proton hopping in GLY, on the surface and in the bulk of Si-ZrP, and hopping on the surfaces of the hydrophilic insoluble silicic acid ( $\text{SiO}_2 \cdot \text{H}_2\text{O}$ ) particles.

A summary of the proton conductivity results reported in this work is shown in Table 1.

### 3.3. FT-IR spectroscopy study

The FT-IR spectra obtained for the ZrP/PTFE/GLY, Si-ZrP/PTFE/GLY and S-ZrP/PTFE/GLY composite membranes are shown in Fig. 9. All composite membranes were prepared at a GLY/ZrP mass ratio of 0.4 and Si/P or S/P mass ratios of 0.004. The spectra of composite membranes revealed characteristic peaks (bands) and shoulders. The characteristic peaks for the phosphate group at 1150 and 1200  $\text{cm}^{-1}$ , are attributed to the P-O asymmetric stretching in the  $\text{PO}_4$  group [21]. The P-O asymmetric stretching peaks were sharp and observed in all samples spectra. The shoulder at 970  $\text{cm}^{-1}$  for the ZrP/PTFE/GLY membrane sample is a characteristic of the P-OH stretching bond [21,22]. The shoulder appeared at

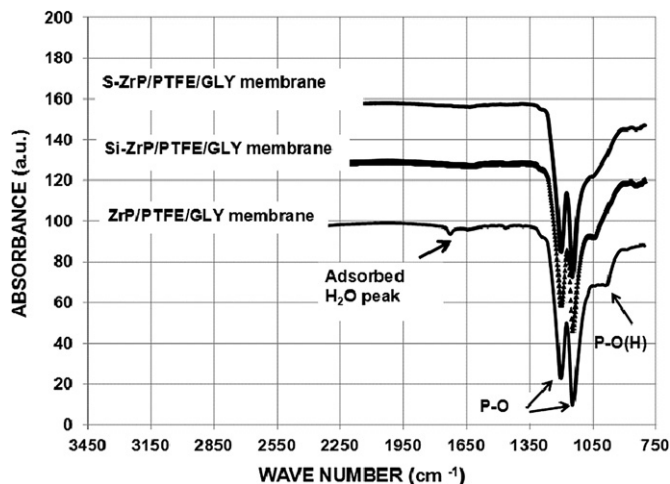
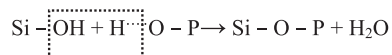


Fig. 9. FT-IR spectra of composite membranes, ZrP/PTFE/GLY, Si-ZrP/PTFE/GLY and S-ZrP/PTFE/GLY, all at GLY/ZrP mass ratio of 0.4, Si/P and S/P mass ratios of 0.004.

1690  $\text{cm}^{-1}$  in the unmodified ZrP/PTFE/GLY composite membrane is a characteristic of bulk water [23]. In general, the FT-IR spectra suggest that no major changes observed on the basic chemical structure of the ZrP material when S or Si replaced a minor amount of P in the ZrP. One change is observed on the shoulder at 970  $\text{cm}^{-1}$  in the unmodified ZrP/PTFE/GLY composite membranes. This shoulder becomes progressively less strong in the Si–ZrP/PTFE/GLY composite membrane and least evident in the S–ZrP/PTFE/GLY composite membrane. The appearance of the shoulder at 1030  $\text{cm}^{-1}$  in the Si–ZrP/PTFE/GLY membrane sample might have resulted from a chemical interaction between the silicic acid ( $\text{SiO}_2 \cdot \text{H}_2\text{O}$ ) and ZrP in the composite membrane, as explained and reported by Le Van So [23]:



This interaction presented in Eq. (3), might have been taking place in our composite membranes that contained  $\text{SiO}_2 \cdot \text{H}_2\text{O}$  and ZrP ( $\text{Zr}(\text{HPO}_4)_2$ ). Presumably, a Si–O–P bond might have been formed. Another possible explanation for the shoulder at 1030  $\text{cm}^{-1}$  in the Si–ZrP/PTFE/GLY membrane, is that it could be due to the stretching vibrations of the Si–O–Si bond [24].

### 3.4. X-ray diffraction (XRD) studies

The XRD patterns for different composite membranes are shown in Figs. 10 and 11. In Fig. 10, the composite membranes studied were the unmodified ZrP/PTFE/GLY and Si–ZrP/PTFE/GLY composites at variable GLY/ZrP and Si/P mass ratios as indicated on the graph. In the three samples, there is a highly intense peak appeared at  $2\theta \sim 18^\circ$ , in addition to two peaks that appeared at  $2\theta \sim 31.5^\circ$ , and  $2\theta \sim 36.6^\circ$ . These peaks are all characteristics of PTFE [25]. However, the PTFE peaks that appeared at  $2\theta \sim 31.5^\circ$ , and  $2\theta \sim 36.6^\circ$  in the Si–ZrP/PTFE/GLY membranes appear to be more intense than those appeared in the unmodified membranes. The two additional peaks only appeared in the Si–ZrP/PTFE/GLY membranes at  $2\theta \sim 49^\circ$ , and  $2\theta \sim 56^\circ$ . These peaks are characteristics of PTFE [26]. These two peaks were not seen in the unmodified ZrP/PTFE/GLY membranes. One possible explanation for the more intense PTFE peaks, and the appearance of two additional ones in the Si–ZrP/PTFE/GLY membranes could be attributed to the morphology as previously seen in SEM analysis (Fig. 2). More PTFE area was exposed in the Si–ZrP/PTFE/GLY membranes and less coverage (by ZrP) was obtained, hence, more intense peaks of PTFE were observed. Furthermore, the PTFE peaks

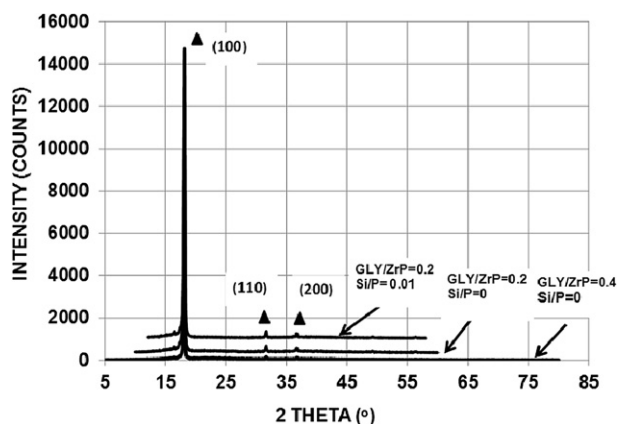


Fig. 10. XRD pattern for ZrP/PTFE/GLY and Si–ZrP/PTFE/GLY composite membranes at variable GLY/ZrP and Si/P mass ratios as labelled.

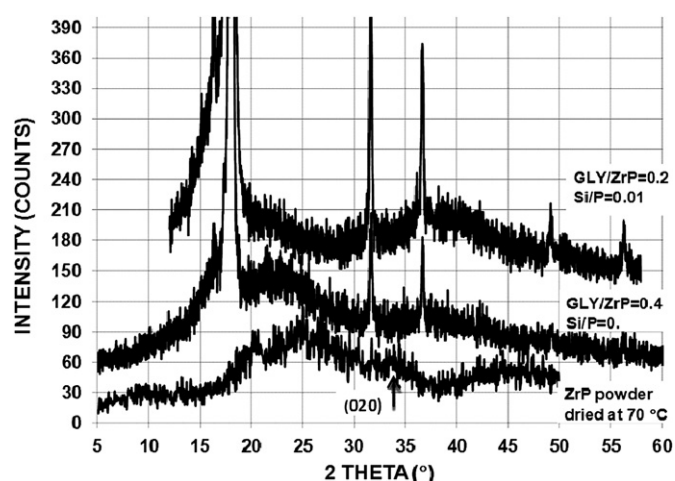


Fig. 11. XRD pattern for ZrP/PTFE/GLY and Si–ZrP/PTFE/GLY composite membranes at GLY/ZrP = 0.2 and Si/P mass ratios as labelled, compared with the XRD pattern for a ZrP powder oven dried at 70 °C.

appeared at  $2\theta \sim 49^\circ$ , and  $2\theta \sim 56^\circ$  in the Si–ZrP/PTFE/GLY membranes might have also existed in the unmodified ZrP/PTFE/GLY spectra, but could not be clearly distinguished from the spectra background. The Miller indices values for the PTFE diffraction peaks in the  $2\theta$  range ( $30\text{--}45^\circ$ ) are also shown in Fig. 10 and are indicated by the triangular markers. The Miller indices assigned for  $2\theta \sim 18^\circ$ ,  $2\theta \sim 31.5^\circ$ , and  $2\theta \sim 36.6^\circ$  are (100), (110) and (200) respectively [26]. This information obtained about the Miller indices suggest that no change occurred to the crystal structure of PTFE when ZrP was added the PTFE pores.

The XRD patterns of the unmodified ZrP/PTFE/GLY and Si–ZrP/PTFE/GLY composites were compared in Fig. 11, with the pattern previously obtained for a ZrP powder, oven dried at 70 °C. With the exception of the PTFE peaks in the composites spectra that appeared at  $2\theta \sim 18^\circ$ ,  $31.5^\circ$ , and  $2\theta \sim 36.6^\circ$ , it can be seen that the materials have amorphous structure. There are two broad peaks in the ZrP powder spectrum at  $2\theta \sim 25^\circ$ ,  $2\theta \sim 33.5^\circ$  and,  $2\theta \sim 45^\circ$  that are consistent with the peaks in the crystalline ZrP [27,28]. Alberti et al. [28] determined a Miller index of (020) for the reflection of ZrP at  $2\theta \sim 33.5^\circ$  as shown in Fig. 11. It is evident that there is a shift in the broad peak appeared at  $2\theta \sim 25^\circ$  in the ZrP powder XRD pattern, into a broad reflection at  $2\theta \sim 22^\circ$  in the unmodified ZrP/PTFE/GLY and in the Si-modified composite membranes. It is not obvious in the Si-modified composite membrane but can be seen with careful examination of the XRD spectrum. There is a broad reflection at  $2\theta \sim 37^\circ$  for both, the unmodified ZrP/PTFE/GLY and the Si–ZrP/PTFE/GLY composite membranes. In general, the XRD spectra suggest that the amorphous ZrP material formed in the composite membranes possess some degree of crystallinity.

## 4. Discussion of results

The morphology and the size of ZrP material changed as a result of the addition of silicic acid ( $\text{SiO}_2 \cdot \text{H}_2\text{O}$ ) or sulphuric acid ( $\text{H}_2\text{SO}_4$ ). In the absence of silicic acid or sulphuric acid, the ZrP particles were spheres with (250–500) nm in diameter. In contrast, plate-like particles of 1–5  $\mu\text{m}$  were formed when “S” or “Si” was present as shown in SEM images.

Porosity is one of the important features of the membranes containing either sulphuric acid or silicic acid. The dense ZrP/PTFE/GLY membranes (Fig. 1a) became porous membranes when either



sulphuric acid (Fig. 1c) or silicic acid (Figs. 1b and 3c, d) was used during preparation. In some membrane samples (Fig. 2e), poor coverage of PTFE, by the modified ZrP material was observed. In a fuel cell, such porosity will permit the undesirable crossover of gases between the anode and the cathode. Composite membranes should be densely packed with particles to prevent gas crossover. The high proton conductivity reported for the Si-modified membranes, combined with their porous structure nature; make them good candidates for catalyst layer supports. Part of the void spaces could be filled with the metal catalyst supported on carbon needed to catalyze the electro-chemical reaction. The presence of void space after adding the catalyst is required to allow the reactants and products to flow.

The XRD patterns confirmed the amorphous nature of the resultant composite membranes. The broad reflections at  $2\theta \sim 22^\circ$  and  $2\theta \sim 37^\circ$  for the unmodified ZrP/PTFE/GLY and the Si–ZrP/PTFE/GLY composite membranes suggest the presence of some degree of crystallinity. The PTFE peaks  $\sim 31.5^\circ$ , and  $2\theta \sim 36.6^\circ$  in the Si–ZrP/PTFE/GLY membranes appeared to be more intense in the Si-modified membranes. Two additional PTFE peaks appeared at  $2\theta \sim 49^\circ$ , and  $2\theta \sim 56^\circ$ . This is consistent with the less coverage of PTFE by the Si-modified ZrP material.

Our hypothesis was that silicic acid would increase the number of OH groups in the ZrP structure and therefore, increase the conductivity. In contrast, sulphuric acid would decrease the number of OH groups, and therefore, decrease the conductivity. The conductivity observed in Fig. 6 supports our hypothesis. The conductivity increased with silicic acid addition, i.e., having more OH groups and decreased with sulphuric acid, i.e., fewer OH groups.

This work reported the conductivity enhancement upon the addition of silicic acid,  $\text{SiO}_2 \cdot \text{H}_2\text{O}$ . When silicic acid was in solution with phosphoric acid, at Si/P ratios of 0.004, it is possible that some of the “P” atoms in ZrP might have been replaced by some “Si” atoms. This increased the number of OH groups, therefore, provided more paths for the protons to hop. Proton conductivity enhancement might have been also caused by the possible formation of the Si–O–P bond, and the formation of water as seen in Eq. (3), thus, providing more water molecules and multiple paths for proton hopping.

When part of the silicic acid was in solution with phosphoric acid and, the other portion was in suspension, i.e., at Si/P mass ratio of 0.01, further enhancement in proton conductivity was observed. The proton conductivity increased reaching a maximum of ( $0.073 \text{ S cm}^{-1}$ ).  $\text{SiO}_2 \cdot \text{H}_2\text{O}$  is a hydrophilic inorganic material. It is possible that the water content of silicic acid may have increased the number of water molecules in the composite membrane. Therefore, the enhancement in proton conductivity is explained by the increased proton hopping in all the preceding paths, in addition to the hopping on the surfaces of the hydrophilic, insoluble  $\text{SiO}_2 \cdot \text{H}_2\text{O}$  particles.

The proton conductivity in the Si–ZrP/PTFE/GLY started to decrease at larger Si/P mass ratios (0.02). This is consistent with what have been previously studied and shown in literature. When an excessive addition of inorganic (e.g.  $\text{SiO}_2$ ) compounds occurred, it led to a decrease in proton conductivity [29]. This result is also consistent with our SEM observations for the Si–ZrP/PTFE/GLY membrane, at Si/P mass ratio of 0.02. The formation of a micron size ZrP particles in some regions, and the poor coverage of PTFE by the modified ZrP material in others, have decreased the total surface area of the ZrP, leading to a decrease in proton conductivity.

## 5. Conclusions

Silicic acid ( $\text{SiO}_2 \cdot \text{H}_2\text{O}$ ) was found to enhance the conductivity of ZrP/PTFE/GLY composite membranes when added to phosphoric

acid prior to the in-situ precipitation reaction. Sulphuric acid was found to have a negative effect on the membranes proton conductivity, decreasing it by orders of magnitude. The conductivity is quite sensitive to the level of OH groups in the ZrP lattice. Both silicic acid and sulphuric acid had an effect on the ZrP particles morphology. In the unmodified GLY/ZrP/PTFE composite membrane, the ZrP material was present as small spheres of (250–500 nm) [15]. When either silicic acid or sulphuric acid was used, the ZrP morphology was changed into a plate-like appearance of a larger size (1–5  $\mu\text{m}$ ). Small additions of other acids dramatically alter the morphology of ZrP/PTFE/GLY membranes.

When silicic acid ( $\text{SiO}_2 \cdot \text{H}_2\text{O}$ ) was in solution with phosphoric acid, the enhancement in proton conductivity may have been caused by the increase in the number of OH groups and in the number of water molecules in the ZrP lattice. This may be explained by the increase in the number of possible proton hopping paths including, ZrP surface, the OH groups in glycerol, and the possible formation of the Si–O–P bond. When part of silicic acid was in solution with phosphoric acid and the other portion was in suspension (i.e. at Si/P mass ratio of 0.01), the enhancement in conductivity was attributed to the preceding reasons plus the proton hopping via the hydrophilic silicic acid particles.

The proton conductivity of the Si–ZrP/PTFE/GLY composite membranes (at Si/P mass ratio of 0.01) reached a maximum of  $0.073 \text{ S cm}^{-1}$  at  $20^\circ\text{C}$ , i.e., 73% of the conductivity of a Nafion membrane. Increasing the Si/P mass ratio to 0.02, caused the proton conductivity to decrease. This was attributed to the poor coverage of PTFE, by the modified ZrP material, hence, the reduction in the total ZrP surface area. When a sample of the Si–ZrP/PTFE/GLY composite membrane was processed at  $200^\circ\text{C}$  in the presence of a steam, under conditions typical of a direct propane fuel cell; the proton conductivity only decreased by 24%.

Although the conductivity measurements reported here are very encouraging, because they approach that of Nafion's. Nevertheless, additional research will be required to develop techniques for preparing Si–ZrP/PTFE/GLY membranes that are dense enough to inhibit gas crossover. However, the values of the conductivity measurements and the porous characteristics reported in this work would make the prepared Si–ZrP/PTFE/GLY material a good candidate for catalyst layer supports for fuel cells applications.

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